

Ultralow friction PTFE/PEEK heterolayer: A new solid lubrication approach toward simplicity

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Abstract: Tribological applications of polytetrafluoroethylene (PTFE) are often limited by technological complexity to overcome its poor wear resistance. Here, a PTFE/polyetheretherketone (PEEK) heterolayer (HL) was proposed and evaluated as a new solid lubrication solution. Pin-on-disk tribometry found the lowest friction coefficient (μ) of 0.031 and ultralow wear for the PEEK/HL under typical conditions. The friction coefficient of the HL surpasses those of the state-of-the-art polymeric coatings/composites by at least 200%, and approaches that of highly lubricated interfaces. Mechanistic investigations revealed multi-length physical and chemical heterogeneity of the HL that best facilitates a tribofilm with high subsurface stability and surface instability. The technological simplicity and robustness of the HL's high lubricity make it a promising new type of solid lubrication toward greater reliability and longevity.

Keywords: ultralow friction; anti-wear; polytetrafluoroethylene (PTFE); heterolayer (HL)

1 Introduction

Polytetrafluoroethylene (PTFE) is widely used in tribological applications because of its self-lubricating characteristics [1, 2], good physicochemical stability, and mature synthesis technique [3]. The self-lubricating characteristic of PTFE is often attributed to its low shear strength, low adhesion, and low surface energy [4]. PTFE structural units consist of tightly packed polymer crystalline slices, with amorphous chains filled between the slices to form a banded microstructure [5]. During frictional shearing, slippages occur between the amorphous regions and the crystalline slices with relatively low resistance [6]. This will draw PTFE fibrils from the polymer surface. Such fibrils tend to adhere to the usually metallic sliding counterface and limit the frictional contact between highly oriented PTFE with low friction coefficients ($\mu \approx 0.1$ – 0.2) [7]. This self-lubricating mechanism of PTFE is referred to as the transfer film formation [8].

PTFE was often used as a solid lubricant sliding against a metallic counterpart to form a self-lubricating system [9]. But the tribological application of PTFE is strongly limited by its poor wear rate (k , $\sim 5 \times 10^{-4}$ mm³/(N·m)) [10, 11]. PTFE is usually reinforced with hard particles/fibers (e.g., metals and ceramics) [12], which tend to improve PTFE's wear resistance at the cost of impairing its lubricity [13]. For example, the inclusion of certain alumina fillers improves the wear resistance of PTFE by over three orders of magnitude but also increases the friction coefficient by nearly 40% (μ , ~ 0.3) [14, 15]. Unfortunately, while Sun et al. [16] and Alam and Burris [17] have made lots of progress in improving the wear resistance of PTFE, limited attention has been paid to reducing the friction of PTFE composites. To reduce the energy consumed in dry lubrication, how to balance friction and wear characteristics of PTFE-related tribosystems remains an important task for tribologists.

Based on Bowden and Tabor's classical theory [18],

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friction coefficient is mainly governed by two types of interactions near the sliding interface: deformation and adhesion. Forming a stable surface film with low surface energy and shear strength could significantly lower friction based on this principle [19]. Mechanistic studies of certain PTFE-based ultralow wear interfaces found structurally and compositionally modified tribofilms near the sliding interface [15, 20, 21]. Using simple surface energy arguments, Ye et al. [22, 23] suggested that (1) highly heterostructured tribofilms effectively reduce the compatibility and weaken the sliding interface, (2) tribofilms (e.g., transfer films on counterface) reduce the interfacial surface energy difference, and (3) interfacial surface energy gradient dictates the direction and magnitude of transfer wear. Van Meter et al. [24] found that by minimizing the interfacial surface energy gradient using a self-mated configuration, the friction coefficient and wear rate of a polyetheretherketone (PEEK)/PTFE composite decreased by nearly 20% and 99.9%, respectively, compared with those of sliding against a metal counterface. An optimum friction coefficient of 0.082 and wear rate of $3 \times 10^{-9} \text{ mm}^3/(\text{N}\cdot\text{m})$ were reported in their study for the self-mated configuration, both of which were near-record for dry sliding polymer solid lubricants.

In general, recent advances in solid lubrication suggest that high-performance tribofilms could be regarded as naturally generated interface heterolayers (HLs) that best reduce adhesion, minimize surface energy gradient, and reduce friction and wear. Tribosystems that best leveraged these effects could achieve unprecedented performance by isolating filler's sometimes conflicting effects on the polymer's surface and subsurface stability [25, 26]. However, in almost all these studies, the initiation, evolution, and stability of tribofilms still rely heavily on the coupling of mechanical, chemical, material, environmental, and sliding parameter (i.e., speed and load) effects that are thermodynamically unstable and difficult to resolve [22, 27].

To transform recent mechanistic breakthrough insights into a more reliable and robust solid lubrication design, we conceive here a new solid lubrication approach, namely, a self-sustaining PTFE/PEEK HL structure. It best leverages (1) the classical adhesive

friction model and (2) interfacial HL's friction and wear-reducing capabilities, and (3) offers additional ease of production and robustness. Briefly, the HL structure was constructed by pre-depositing a thin continuous layer of PTFE on a PEEK substrate through simple frictional sliding. The HL-covered substrate was further slid against a PEEK sample using a three-pin-on-disk configuration. It demonstrated significantly lower friction coefficients (0.031–0.056) and similar ultralow wear rates ($\sim 9 \times 10^{-8} \text{ mm}^3/(\text{N}\cdot\text{m})$) than those of any comparable interface in the literature. Detailed forensic characterizations were conducted, and a tribofilm structure-induced friction and wear reduction model was proposed.

2 Experimental

2.1 Material and HL preparation

PEEK was selected as the counterpart material in this study for its excellent mechanical strength and wear resistance and good compatibility with PTFE. For example, it has been reported in Refs. [24, 28] that PEEK can form a gradient anti-wear structure with PTFE. Driven by van der Waals interactions and stress-induced deformation, PTFE can form an adsorbed film on the PEEK surface during the frictional contact, resulting in the PTFE/PEEK HL formation. A $\Phi 16 \text{ mm}$ hollow cylinder of neat PTFE with an inner diameter of 8 mm was prepared by compression molding at 35 MPa at room temperature, heated to 370 °C for 3 h, and then naturally cooled to room temperature. PEEK samples for HL substrates and counter-sample pins were molded at 55 MPa at room temperature, heated to 360 °C for 3 h in the molds, and then naturally cooled to room temperature. The PTFE powder was PTFE 7C (Teflon) with a reported average diameter of $\sim 38 \mu\text{m}$. The PEEK powder was 450PF (Vicatex) with a reported average diameter of $\sim 48 \mu\text{m}$. The PTFE/PEEK HL is created by sliding a PEEK substrate against a PTFE cylinder in a thrust washer configuration, as illustrated in Fig. 1(a). The PTFE cylinder was pressed against the PEEK disk with a diameter of 35 mm and thickness of 5 mm at the normal load (F_n) of $\sim 900 \text{ N}$ and the sliding velocity (ω) of 79.5 r/min (i.e., linear velocity of 50 mm/s). After 10 min of sliding, a

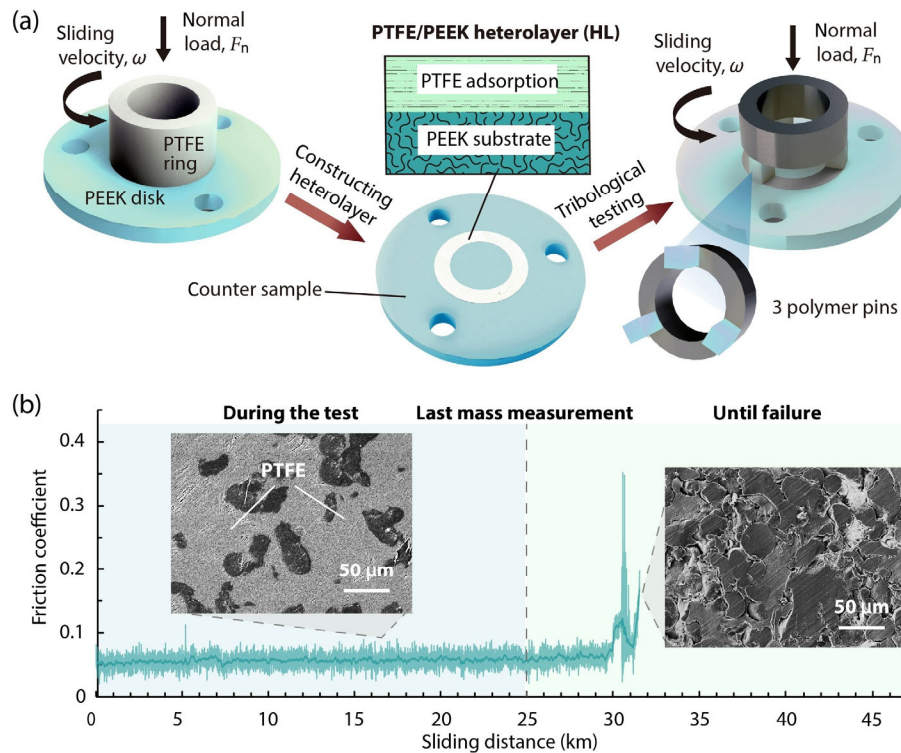


Fig. 1 (a) Thrust washer configuration for constructing PTFE/PEEK HL and pin-on-disk configuration for tribological testing of PTFE/PEEK HL against PEEK counter-sample. (b) Typical friction coefficient evolution of PTFE/PEEK HL up till ultralow friction failed. The scanning electron microscope (SEM) images (the insets in (b)) show the HL surfaces during test and after failure.

PTFE/PEEK HL was formed on the PEEK substrate. In preliminary tests, we found a minimum contact pressure and sliding distance (d) of ~ 3.8 MPa ($\sim 1/6$ of the yield strength) and ~ 15 m, respectively, beyond which a uniform PTFE/PEEK HL can be formed reliably.

2.2 Tribological tests

The tribological properties of the PTFE/PEEK HL and reference samples were tested using the custom-built pin-on-disk tribometer with an in-house modified stage and a data acquisition system, as illustrated in Fig. 1. The HL samples were submerged in water and sonicated for 5 min to remove non-transferred debris and dried at 60°C for 3 h. Before the tribological tests, a short distance of pre-sliding against 800# SiC sandpapers was conducted to the three-pin PEEK counterpart to promote a uniform contact pressure distribution. The contact area (A) of each pin is $4\text{ mm} \times 4\text{ mm}$. Tests were imperatively stopped if the wear volume of a tested pin is over 100 mm^3 . A normal contact pressure of 6.0 MPa ($F_n = 288\text{ N}$) and a sliding

speed of 50 mm/s were applied until failure ($\mu > 0.2$), as illustrated in Fig. 1(b).

Interrupted mass measurements were performed at certain intervals to measure the wear volume of the pin or the substrate sample (Δm_{loss}) using a scale ($\pm 10\ \mu\text{g}$). The last mass measurement of each test was usually at about the 140th hour ($d \approx 25\text{ km}$). The total life of the PTFE/PEEK HL was tested to be 170–220 h without significant increase of the friction coefficient based on five repeat endurance tests at 6.0 MPa and 50 mm/s (Fig. 1(b)). The k is calculated by Eq. (1):

$$k = \frac{\Delta m_{\text{loss}}}{\rho F_n d} \quad (1)$$

where ρ ($= 2.2\text{ mg/mm}^3$) is the predetermined PTFE density, F_n is the normal load (N), and d is the sliding distance (m). The wear rates were calculated using one mass loss measured at and before the interval to better evaluate the run-in wear characteristics. Steady-state wear rates were calculated using the last three wear measurements. The uncertainty analysis of wear rates uses a Monte Carlo method developed by Burriss

and Sawyer [29]. The μ is the ratio of the measured force parallel to the sliding direction (i.e., the product of torque and moment arm) to the normal load. The laboratory temperature and humidity are constantly controlled during the tests at ~ 25 °C and $\sim 40\%$ relative humidity, respectively. Each test was repeated at least three times.

The friction sensitivity of PTFE/PEEK HL samples to sliding speed in the range of 2–300 mm/s was investigated. During the tests, the interfacial temperature rise due to frictional heating was monitored using an infrared (IR) camera (H16, HIKVISION; ± 1 °C). In our preliminary tests, the friction performance of PTFE/PEEK HL samples was insensitive to the applied load in the range of 2.0–8.0 MPa. To better compare with Refs. [15, 24, 30], this study presents detailed results under the normal load of 6.0 MPa and sliding speed of 50 mm/s.

2.3 Analyses of surfaces and tribolayers

The morphological and chemical characterizations of the prepared PTFE/PEEK HL were performed using a three-dimensional (3D) laser scanning confocal microscope (VK-X100, KEYENCE) and an SEM (Gemini 500, ZEISS) before the tribological tests. The unworn sample was submerged in liquid nitrogen and bent to create a cross-sectional surface. An X-ray diffractometer (D/MAX2500VL/PC, Rigaku) was utilized in reflection mode (Cu K α radiation, $\lambda = 1.54$ Å) to obtain the X-ray diffraction (XRD) patterns to confirm the crystal structures of the PTFE/PEEK HL. The Fourier transform infrared (FTIR) spectra of surface samples were measured using an attenuated total reflectance (ATR) sampling accessory equipped with a single bounce diamond crystal on a spectrometer (Nicolet 6700, Thermo Scientific), resulting in a spectrum that samples the selected $200 \mu\text{m} \times 200 \mu\text{m}$ surface. Each presented FTIR spectrum is the average of 64 scans. The interfacial structures of the tribolayers were further characterized using the X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific) measurements combined with argon ion etching techniques. The XPS elemental results were averaged from three areas near the center of the worn HL surface and counterface.

2.4 Simulation

Directly observing the dynamic behavior of the tribolayers can provide important insights into their functionality during sliding. The molecular dynamics simulation was performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code developed at Sandia National Laboratory, USA. As suggested in Refs. [28, 31], the consistent valence force field (CVFF) was used to calculate the atomic and molecular interactions. The Open Visualization Tool (OVITO) was used to visualize the simulation models. The size of the simulation boxes is $40 \text{ \AA} \times 40 \text{ \AA} \times 150 \text{ \AA}$. PTFE ($\text{C}_{15}\text{H}_6\text{F}_{26}$, with methyl ends), PEEK ($\text{C}_{26}\text{H}_{18}\text{O}_4$), and carboxylated PTFE ($\text{C}_{15}\text{H}_2\text{O}_4\text{F}_{26}$, with carboxylic ends) molecules were built for building the polymer models. The periodic tribolayer models of PTFE, PEEK, and carboxylated PTFE with the size of $\sim 40 \text{ \AA} \times 40 \text{ \AA} \times 25 \text{ \AA}$ were generated using a Monte Carlo method. Consistent with the experimental results, the periodic polymer bulks were layered as PEEK, carboxylated PTFE, PTFE, carboxylated PTFE, and PEEK sequentially. A 25 \AA of vacuum separated the simulated periodic surfaces from the perpendicular adjacent.

The interatomic Lennard–Jones parameters are determined using the arithmetic combining rule, and the cutoff distance for all interactions is 10 \AA . The velocity Verlet algorithm was used to solve the equation of motion. The geometry of interface models was optimized with the energy convergence accuracy of 10^{-6} kcal/mol. Before shearing, 200 ps of NPT structural relaxation was performed at the consistent temperature of 298 K and pressure of 0.2 GPa. Nose–Hoover Langevin and Berendsen barostat algorithms were applied during the simulation in temperature and pressure control. The Ewald summation method was used to calculate the electrostatic interactions. The rigid layer of the PEEK substrate with a thickness of 25 \AA is fixed. The top layer of the PEEK slider is forced to slide at a constant speed of 0.2 \AA/ps under the load of 0.2 GPa with a total simulation time of 400 ps. The atomic layers of carboxylated PTFE and PTFE can move freely.

The interaction strength (E_{int} (eV/nm²)) between polymer layers was calculated to investigate the undying mechanism for the tribolayers' dynamic

behavior. For example, the PEEK-carboxylated PTFE model and their adsorbed structure models are geometrically optimized and relaxed at the consistent temperature of 298 K and pressure of 0.2 GPa for 100 ps. The interaction energy (E_{abs} (eV)) of model 1 (e.g., PEEK) and model 2 (e.g., carboxylated PTFE) are calculated as

$$E_{\text{abs}} = E_1 + E_2 - E_{12} \quad (2)$$

where E_1 , E_2 , and E_{12} are the structural energy of polymer model 1, polymer model 2, and the adsorbed structure of two polymers, respectively. The E_{int} is the ratio of E_{abs} to the interaction area of bulk models.

3 Results

3.1 HL structure characterization

We first investigated the morphological and chemical characteristics of the PTFE/PEEK HL. Figure 2(a)

shows that a layer of adsorption film was formed on the PEEK surface after sliding against PTFE. Laser confocal measurement results suggest that the rubbed area has a relatively higher roughness than the PEEK substrate (Fig. 2(b)). This could be related to the shear-induced deformation of transfer films. The SEM measurements were conducted for the area marked with a red dotted box (Fig. 2(a)) and revealed that the layer of adsorption film is highly continuous with strong directionality (Fig. 2(c)). The energy dispersive spectroscopy (EDS) elemental mappings (Fig. 2(d)) find that fluorine concentrates on the adsorption films. Figures 2(e) and 2(f) are the cross-sectional HL SEM and EDS images, respectively, showing a clear boundary between the PTFE adsorption layer and the PEEK substrate. The average thickness of the PTFE layer was estimated to be $\sim 12.3 \mu\text{m}$ according to the increase of mass. This is in accordance with the film thickness measured in the cross-sectional images ($\sim 10.6 \mu\text{m}$). The IR spectra of the PTFE/PEEK HL and

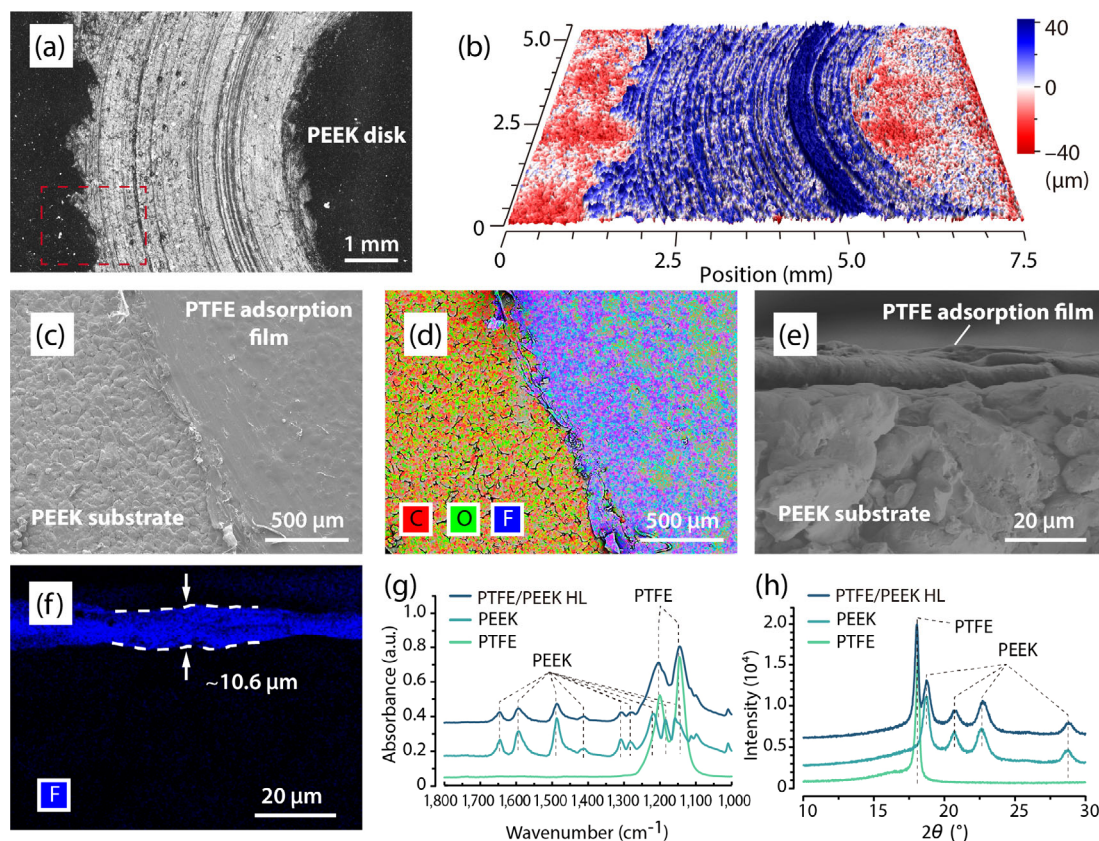


Fig. 2 (a) Optical micrograph, (b) laser-scanning height imaging, and (c) SEM image of the as-prepared PTFE/PEEK HL surface. (d) EDS elemental mapping of carbon, oxygen, and fluorine corresponding to the SEM measurement. (e) SEM image and (f) fluorine elemental mapping of cross-sectional HL sample. (g) FTIR spectra and (h) XRD patterns of PTFE/PEEK HL and neat polymer references.

reference polymers are shown in Fig. 2(g). The peaks at 1,143 and 1,199 cm^{-1} are characteristic of PTFE molecules and correspond to the symmetric and asymmetric stretching of the CF_2 units [24], respectively. The peaks in the range of 1,147–1,194 cm^{-1} are characteristic of aromatic C–H deformation in PEEK [15]. The peaks at 1,645, 1,593, 1,487, and 1,411 cm^{-1} are also markers of PEEK [32]. The peaks at 1,218 cm^{-1} correspond to carbonyl stretching, ascribed to the PEEK substrate [24]. The XRD results show that only PTFE and PEEK appear in the HL structure (Fig. 2(h)).

3.2 Frictional behavior and speed sensitivity

The PTFE/PEEK HL exhibits an ultra-low friction coefficient of ~ 0.054 when sliding against a PEEK counter-sample, the lowest among the four tested tribosystems at comparable conditions (Fig. 3(a)). The PTFE adsorption layer exhibits excellent lubricating stability during sliding against the relatively hard PEEK surface. Low μ values (< 0.1) can be observed in the initial sliding of PEEK-on-PEEK tribopairs. Frictional heating causes a large rise of the interfacial temperature (ΔT) of ~ 130 °C after ~ 20 min. This resulted in a surging of friction with $\mu > 0.40$, which forced the termination of the test. While in the case of PEEK-on-HL, PEEK-on-PTFE, and PTFE-on-PTFE tribosystems, the steady-state interfacial temperature rises were maintained at $\Delta T \approx 30$ – 40 °C. This implies that the presence of PTFE is important for improving the self-lubricating performance and reducing frictional heating in polymer-on-polymer systems. Tribological responses of PEEK and PTFE to varying temperatures

are interesting topics well addressed in Refs. [33, 34]. In this paper, the PTFE/PEEK HL structure is designed using the unique tribological characteristics of the two materials.

In the speed sensitivity tests, we found that PEEK-on-HL exhibits the lowest friction coefficient of ~ 0.031 at the sliding velocity of 2 mm/s, as shown in Fig. 3(b). To our best knowledge, the PTFE/PEEK HL has the lowest friction coefficient among various state-of-the-art PTFE-based solid lubrication interfaces under comparable pressure and velocity conditions (pv values) [24, 35–38], as listed in Table 1. Besides, PEEK-on-HL systems exhibits a similar speed sensitivity to the PEEK-on-PTFE and PTFE-on-PTFE. It is highly suggested that the self-lubricating characteristic of PTFE plays an important role in the tribological performance of PTFE/PEEK HL [39]. This will be further investigated in Section 4.2.

3.3 Wear performance and wear track's evolution

The wear behavior of PTFE/PEEK HL and PEEK counter-samples was investigated to probe the stability of the PTFE/PEEK HL structure during sliding. The average volume of PTFE transfers in the HL is ~ 1.85 mm^3 . The wear volume of PTFE/PEEK HL is ~ 0.21 mm^3 after 0.1 km of sliding, as plotted in Fig. 4(a). According to Eq. (1), the wear rate of HL during the initial 0.1 km is $\sim 7.47 \times 10^{-7}$ $\text{mm}^3/(\text{N}\cdot\text{m})$. Further to 10 km, the volume of the HL sample lost 0.29 mm^3 , which is merely 1.5 times higher than that of the initial 0.1 km test. This indicates that the wear resistance of the HL was significantly improved during

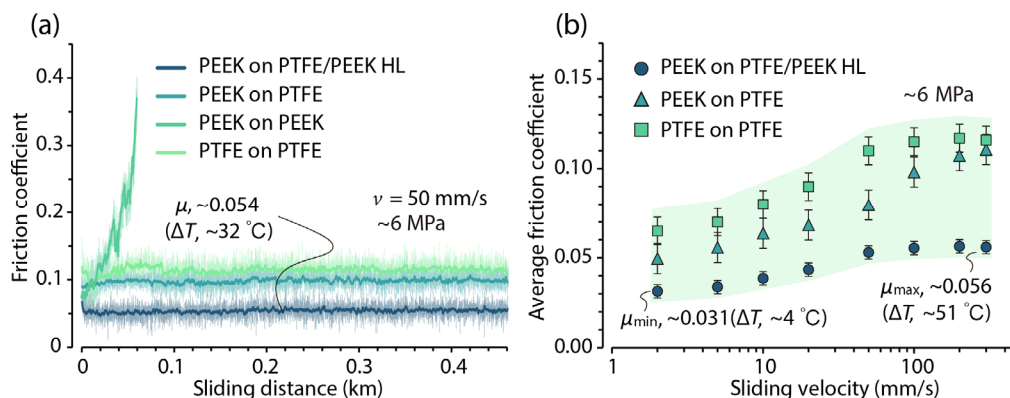


Fig. 3 (a) Temporal evolution of μ during tribological tests of PEEK-on-HL, PEEK-on-PTFE, PEEK-on-PEEK, and PTFE-on-PTFE tribopairs. (b) Average μ plotted as a function of sliding velocity for PEEK-on-HL, PEEK-on-PTFE, and PTFE-on-PTFE systems. Each data point represents the average of three individual repeats, and the error bars represent the 95% confidence interval.

Table 1 Summary of tribological results in our study compared with those of the state-of-the-art and typical solid lubrication designs. The pv values were calculated according to the Hertzian contact model and provided experimental details from Refs. [24, 35–38].

Lubrication type	Substrate	Counter-sample	Average μ	Test configuration	pv value (MPa·m/s)	Ref.
PTFE/PEEK HL	PEEK	PEEK	~0.031–0.056	Pin-on-disk	0.012–1.8	This study
PTFE/MXene coating	Silicon	Steel	~0.15	Ball-on-disk	~0.54	[35]
TiN–MoS ₂ /PTFE coating	Cemented carbide	Silicon carbide	~0.10	Ball-on-disk	~1.0	[36]
Polydopamine (PDA)–Ag/PTFE	Steel	Steel	~0.08	Ball-on-disk	<10.4	[37]
Self-lubricating	30 wt% PEEK/PTFE	30 wt% PEEK/PTFE	~0.08	Pin-on-disk	0.3	[24]
Self-lubricating	Steel	30 wt% PEEK/PTFE	~0.11	Pin-on-disk	0.3	[24]
Self-lubricating	Steel	PTFE	~0.18	Pin-on-disk	0.3	[24]
Self-lubricating	Steel	PEEK	~0.29	Pin-on-disk	4.0	[38]

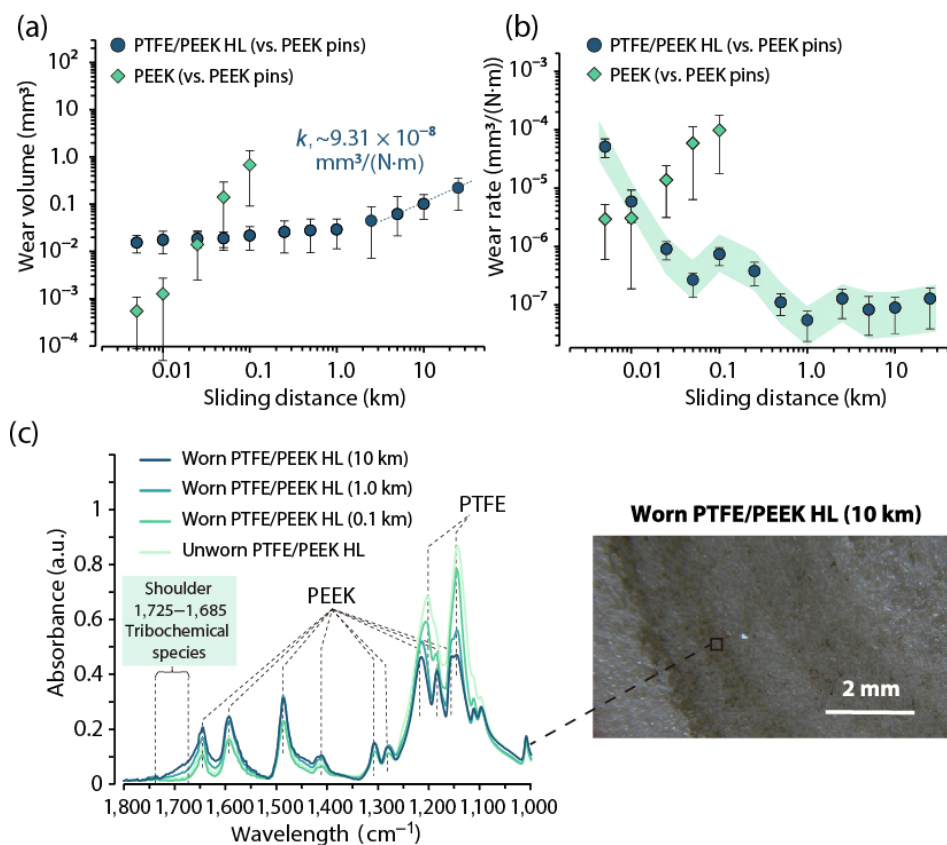


Fig. 4 (a) Wear volumes and (b) calculated wear rates of disk samples of PTFE/PEEK HL against PEEK and PEEK against PEEK over $d = 25$ km. (c) ATR-IR spectra of worn surfaces of PTFE/PEEK HL run against PEEK pins and unworn HL reference. The inset shows the worn PTFE/PEEK HL after 10 km sliding.

the sliding test, which is consistent with the wear rate calculations, as shown in Fig. 4(b). The steady-state wear rate is calculated to be $\sim 9.31 \times 10^{-8} \text{ mm}^3/(\text{N}\cdot\text{m})$, reaching the ultra-low wear materials [15, 24, 40]. The total life of the PTFE/PEEK HL structure is tested to be 170–220 h without lubricant replenishment,

according to five infinite duration tests at 6 MPa and 50 mm/s. In the case of PEEK-on-PEEK, the substrate showed a low wear rate initially. But its wear rate increased significantly with the increasing friction coefficient corresponding to Fig. 4(a).

The FTIR spectra were obtained for the worn surfaces

of the PTFE/PEEK HL and the unworn reference. The absorbance spectra of worn HL samples after 0.1, 1, and 10 km sliding are plotted in Fig. 4(c). All spectra were normalized to have the same total integral area. References [41, 42] found that PTFE can experience a series of tribochemical reactions, i.e., mechanochemical reactions, under the activation of mechanical stresses. The tribochemical products would react with water and oxygen at an ambient condition, resulting in the carboxylated PTFE formation and crosslinked, strengthened tribofilms [15, 16]. The spectral identification of new tribochemical species in the region between 1,400 and 1,725 cm^{-1} was challenging in the worn HL surface due to the absorbance of the PEEK carbonyl groups and intrachain ether bonds overlapping with those of perfluorinated carboxylic acid groups [15, 16, 24]. Compared to the unworn HL sample, there appeared increasingly obvious shoulder peaks between 1,685 and 1,725 cm^{-1} as the d increased. References [43–46] have observed these new peaks

and correlated them with tribochemical products in ultra-low wear PTFE-based composites.

The HL structure also reduced the wear of the counter-samples. Compared to PEEK pins rubbed with neat PEEK, the samples rubbed against PTFE/PEEK HL lost volume of 0.04 mm^3 after 0.1 km of sliding, which is approximately 3% of that of PEEK-on-PEEK substrate, as shown in Fig. 5(a). The HL counter-sample's wear rates at 0.1 km and the steady-state are $\sim 9.21 \times 10^{-8}$ and $\sim 4.66 \times 10^{-8}$ $\text{mm}^3/\text{N}\cdot\text{m}$, respectively (Fig. 5(b)). The wear rate of the PEEK–PEEK counter-sample increases rapidly with sliding, which is consistent with the wear trend of the substrate. According to the FTIR results (Fig. 5(c)), no obvious tribochemical change could be found on the worn PEEK counterface. But this does not mean that there is no tribochemical reaction near the pins' surfaces. Since the detection depth of the ATR-IR is typical within a few microns (ca. 0.5–3 μm) below the surface [47], the nanoscale tribochemical product is difficult

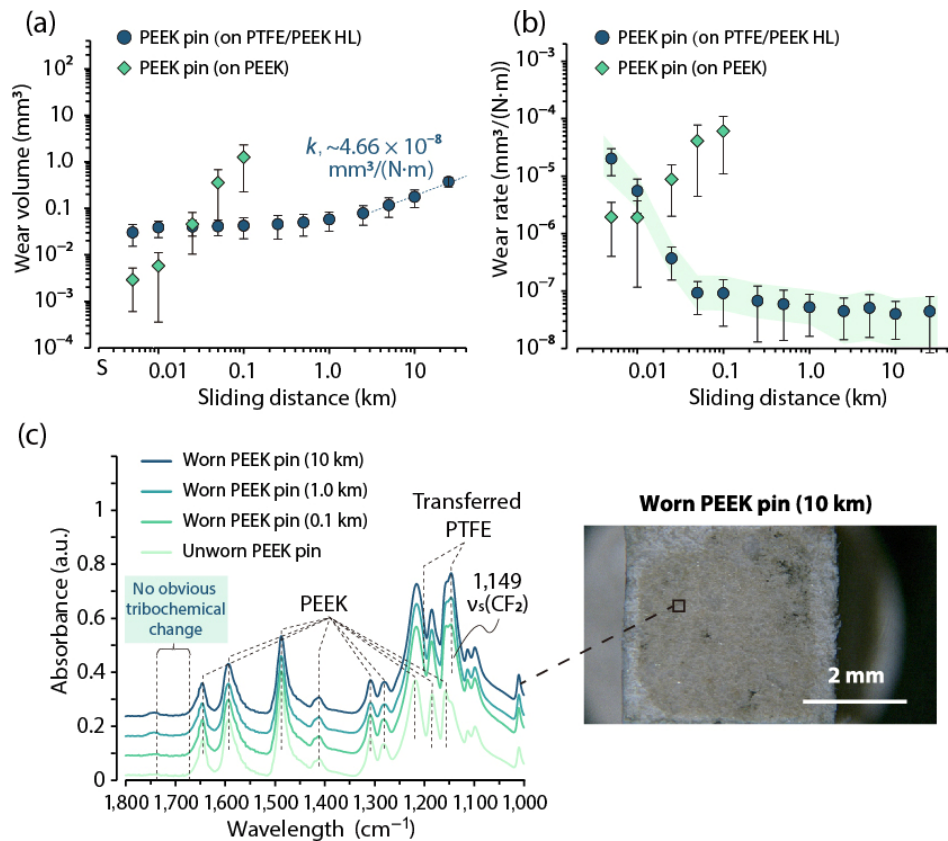


Fig. 5 (a) Wear volumes and (b) calculated wear rates of counter-sample pins of PEEK-on-PTFE/PEEK HL and PEEK-on-PEEK over $d = 25$ km. (c) ATR-IR spectra of worn surfaces of PEEK pins and unworn PEEK reference. The inset shows the worn PEEK pin after 10 km sliding.

to detect using this method. More details of tribochemistry are further investigated using the surface analytical technologies hereafter.

The SEM measurements were performed for the as-prepared and 0.1 km of worn HL samples, as shown in Figs. 6(a) and 6(b), respectively. The as-prepared, unworn PTFE adsorption film exhibits a high continuity and an average coverage of $\sim 85\%$, estimated using a threshold method [8, 48]. After 0.1 km sliding, the average coverage of PTFE decreased by $\sim 43.7\%$. While the sliding of 0.1 km only caused $\sim 0.21 \text{ mm}^3$ wear volumes of PTFE/PEEK HL, which are $\sim 11.3\%$ of the total volume of PTFE transfer. The wear volume does not match the change in film coverage. It is hypothesized that the disappeared PTFE films are not worn out but stored near the sliding interface by shear-induced deformation.

The EDS elemental measurement results partially support this hypothesis. The elemental mappings of carbon, fluorine, and oxygen were obtained from the worn PTFE/PEEK HL after a test of 25 km. The SEM image and its corresponding EDS images are shown in Fig. 6(c) and Figs. 6(d)–6(f), respectively. With the high-energy electron beam, the EDS measurement has a large interaction volume and can detect the elemental distribution in the subsurface within several microns. The carbon-enriched areas (Fig. 6(d)) are mainly PEEK asperities due to their benzene rings, consistent with

the SEM observation. The presence of fluorine marks the interfacial PTFE. Interestingly, obvious fluorine signals overlapped in the PEEK-appeared areas, indicating an interpenetrating surface structure of PEEK and PTFE, which may best facilitate the PTFE as lubricant reservoirs. This partially explains the low wear of the PTFE layer and its long-term lubricating functionality. Figure 6(f) suggests that there is oxygen also appearing near the PTFE reservoirs. But it cannot be determined whether those oxygen signals are from PEEK or carboxylated PTFE, which will be further investigated in Section 4.

4 Discussion

4.1 Mechanistic discussion on HL formation

A possible reason for the transfer film continuity could be the PTFE polymer's high creep. Despite its excellent chemical stability, PTFE typically undergoes large plastic deformation under continuous loading, known as its high creep or cold flow [49]. The sliding contact results in the defect appearing near the worn surface of PEEK. These defects allow PTFE polymers to remain on the PEEK surface and form a layer of adsorption films through mechanical interlocking, as illustrated in Fig. 7(a). Such phenomena barely occur on hard metal or ceramic surfaces. Besides,

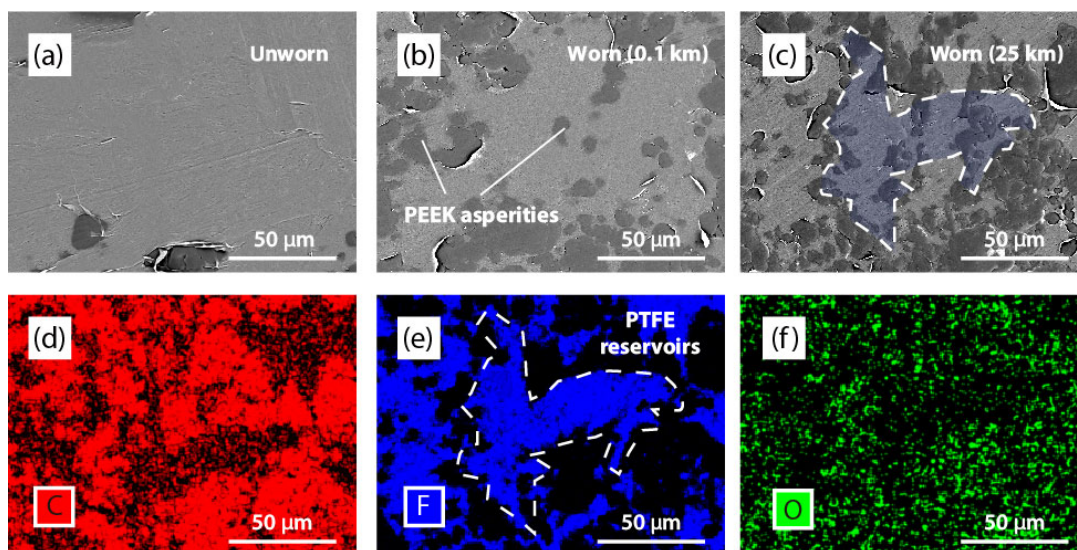


Fig. 6 SEM images of (a) unworn PTFE/PEEK HL surface, (b) worn PTFE/PEEK HL surface after 0.1 km sliding, and (c) worn PTFE/PEEK HL surface after 25 km sliding. EDS elemental mappings of (d) carbon, (e) fluorine, and (f) oxygen obtained from the worn PTFE/PEEK HL surface after 25 km sliding.

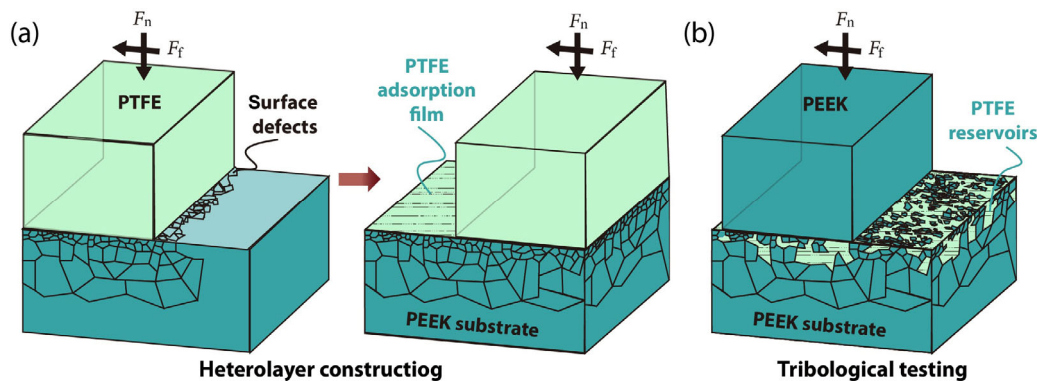


Fig. 7 Schematic of (a) HL construction and (b) PTFE reservoir formation during tribological testing. Note: F_f and F_n are the friction force and normal load, respectively.

stress-induced creep may allow the PTFE films to be stored in the contact subsurface as lubricant reservoirs during sliding rather than squeezed out (Fig. 7(b)).

4.2 Mechanistic discussion on ultra-low friction performance

Our results demonstrate that the lubricity of the PTFE/PEEK HL structure is superior to those of the PTFE–PEEK and PTFE–PTFE in polymer-on-polymer configurations. According to the report of van Meter et al. [24], the friction performance of PTFE/PEEK HL was also better than the best of self-mated PTFE composites under comparable test conditions. According to the classical adhesive friction theory, a smaller contact area or lower shear strength of the tribolayer can potentially reduce the μ as [50]:

$$\mu = \frac{F_f}{F_n} \propto \frac{\tau A}{F_n} \quad (30)$$

where F_f and F_n are the friction force and normal load, respectively, and τ and A are the shear strength of the tribolayer and the contact area, respectively. We suspect that the PTFE/PEEK HL achieved the lowest friction coefficient by independently and simultaneously reducing τ and A . In other words, the HL layer provides low adhesion and shear strength, and the PEEK substrate provides high contact stiffness and limits the contact area [18, 51].

To study the mechanism of ultra-low friction, the microstructures of tribolayers and the surface mechanics need to be investigated. Since the XPS measurements can be used in nanometer-scale surface analysis, we

first performed the F 1s XPS measurements on the unworn HL, the worn HL, and the worn counterface. Figure 8(a) reveals that the top surfaces of the worn HL and counterface are enriched by long-chain PTFE, consistent with the peaks of 689 eV [52]. The XPS and argon ion etching techniques were combined to probe the element content changes with depth near the contact surfaces to further investigate this PTFE-enriched region's depth. The area with a fluorine concentration of >10% is the PTFE-enriched region. For the worn PTFE/PEEK HL surface, Fig. 8(b) suggests that the PTFE-enriched region is approximately 180 nm near the surface, assuming an etching rate of 0.15 nm/s. The fluorine content gradually decreases, while the carbon and oxygen contents increase with the etching depth, showing the transition from the PTFE-enriched surface to the PEEK substrate. In the case of the worn counterface, its PTFE-enriched region is relatively thinner than that of HL, with a thickness of ~120 nm (Fig. 8(c)).

Another factor that could affect the friction performance of PTFE/PEEK HL is the real contact area. Since the real contact area is closely correlated to surface deformation, we first investigated the reduced moduli of the polymer surfaces using the AFM indentation technique. Based on Ref. [53], the average reduced moduli of the worn PEEK, HL, and PTFE reference surfaces were measured to be ~2.42, ~1.93, and ~0.54 GPa, respectively, under an indentation depth of ~500 nm. Noticeably, although adsorbed PTFE films partially reduce the modulus of the PEEK, the PTFE/PEEK HL has a relatively higher modulus than PTFE due to the substrate effect. Figure 8(d)

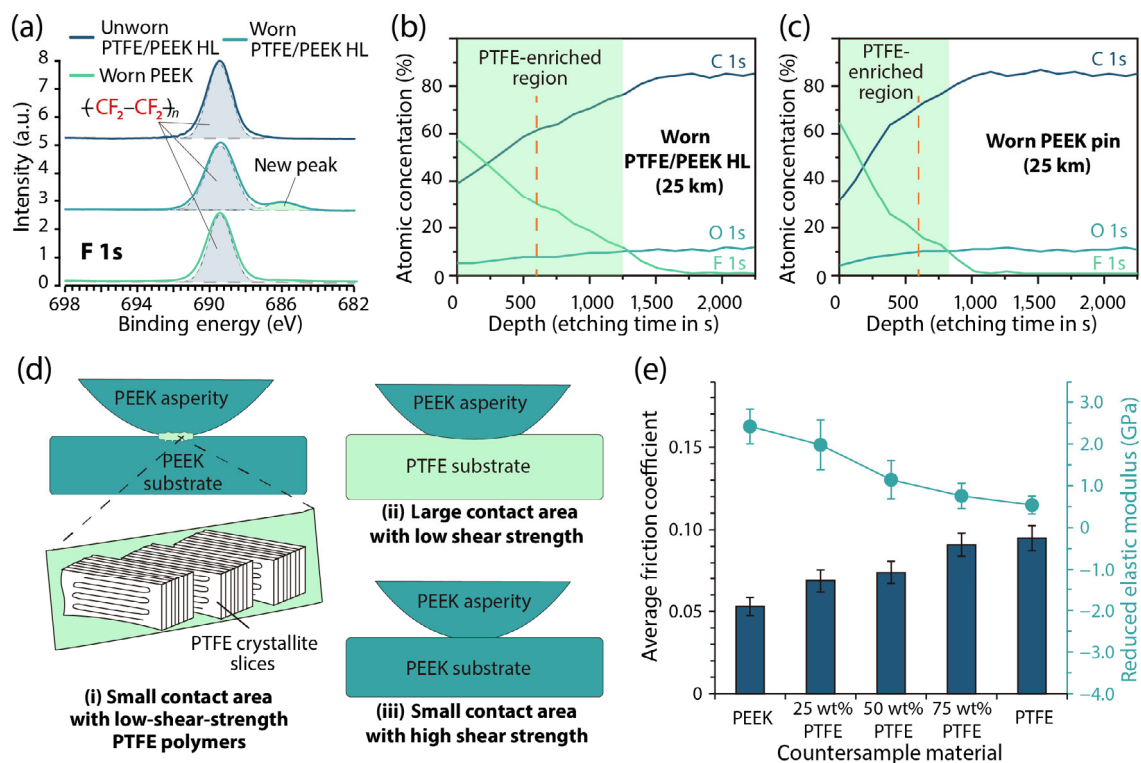


Fig. 8 (a) High-resolution XPS spectra of F 1s measured on unworn PTFE/PEEK HL, worn PTFE/PEEK HL, and worn PEEK pin surfaces. Atomic concentrations of (b) worn PTFE/PEEK HL and (c) worn PEEK pin surfaces plotted as a function of depth represented by etching time (in s). (d) Schematic diagrams of equivalent contact of PEEK-on-PEEK, PEEK-on-PTFE, and PEEK-on-PEEK tribosystems. (e) Average friction coefficients of PTFE/PEEK HL sliding against PEEK, PTFE, and various PTFE/PEEK composite counter-samples. The reduced moduli of those counter-samples were provided.

shows the schematics of three typical frictional contact systems. In the PEEK-on-PEEK system lubricated by a PTFE layer (case (i)), the real contact area is smaller than that of the PEEK-on-PTFE system (case (ii)) due to the lower modulus of the PTFE substrate. The real contact area of PEEK-PEEK is smaller than that of the PEEK-on-PTFE configuration under the identical load condition. But due to the high internal friction of PEEK-on-PTFE (case (iii)), it cannot achieve a low friction as PTFE/PEEK HL does.

To test this hypothesis, we further investigate the effects of contact modulus on the friction performance of PTFE/PEEK HL. The 25, 50, and 75 wt% PTFE-filled PEEK composites were prepared based on Ref. [24]. The mechanical properties of PEEK can be regulated without introducing other materials by this method. These composites were then used as counter-sample pins for tribological testing. The average friction coefficients and measured moduli are shown in Fig. 8(e), showing the increasingly high friction

coefficient with the smaller counter-sample modulus and the increase of PTFE content. This indicates that the HL friction performance is related to the reduced modulus of tribopairs, which partially confirms our mechanistic hypothesis.

4.3 Gradient structure of tribo-interface

PTFE/PEEK HL formation and lubricating mechanisms have been in Sections 4.1 and 4.2. One unresolved issue is the microstructure of the HL tribo-interface. Understanding the structure of this low-friction and low-wear tribosystem can be extremely useful to the further development of new tribological coatings or new types of lubricants. The structure of tribolayers was analyzed using the high-resolution XPS measurements. The C 1s, O 1s, and F 1s XPS spectra of the worn top surfaces (Top surf.) and their subsurfaces (Subsurf., ion-etched after 10 min) were obtained, as shown in Figs. 9(a), 9(b), and 9(c), respectively. The spectra of the unworn PEEK are also

shown as references. Figure 9(a) shows that the C 1s spectrum of PEEK is characterized by two main peaks at 284.7 and 286.3 eV, which are assigned to be the benzene C–C and the ether C–O bonds of PEEK, respectively [54]. The O 1s spectra of PEEK have two main peaks at 531.3 and 533.1 eV (Fig. 9(b)), corresponding to the carbonyl and ether bonds, respectively. PTFE molecules cover the worn PEEK counterface after the 25 km of sliding against PTFE/PEEK HL, which are consistent with the C–F bond peak at 292.2 eV and the skeleton C–C bond peak at 284.8 eV (Fig. 9(a)). This is further confirmed by the presence of the C–F bond (689.2 eV, Fig. 9(c)). Noticeably, the high-resolution C 1s spectra of the subsurface show newly appeared C–O bond signals of carboxylic acid carbonyl and hydroxyl groups at the 289.2 and 287.2 eV (Fig. 9(a)), respectively. This is further confirmed by the newly appeared 532.2 and 533.7 eV peaks, as shown in Fig. 9(b), corresponding

to the carbonyl and hydroxyl groups, respectively [55]. The F 1s spectra of the subsurface show a new peak at 686.4 eV, which has not been previously described in the literature. According to the C 1s and O 1s spectra, we suspect that the new signal peak is related to the formation of carboxylic acid groups.

The high-resolution XPS spectra of the worn surface of PTFE/PEEK HL show symmetry with those of the top surface, as shown in Figs. 9(d)–9(f). Before the tribological test, the HL surface was mainly PTFE adsorption films and PEEK asperities, as marked in the spectra. After sliding with PEEK counter-samples, the top and sub-surfaces of PTFE/PEEK HL contain abundant tribochemical products, including increased CF₃ ends (294.3 eV, Fig. 9(d)) and the presence of carboxylic acid groups (Figs. 9(d) and 9(e)). The increase of CF₃ ends near the surface proves that the PTFE polymers undergo friction-induced chain breaks, consistent with Refs. [16, 56]. The appearance of

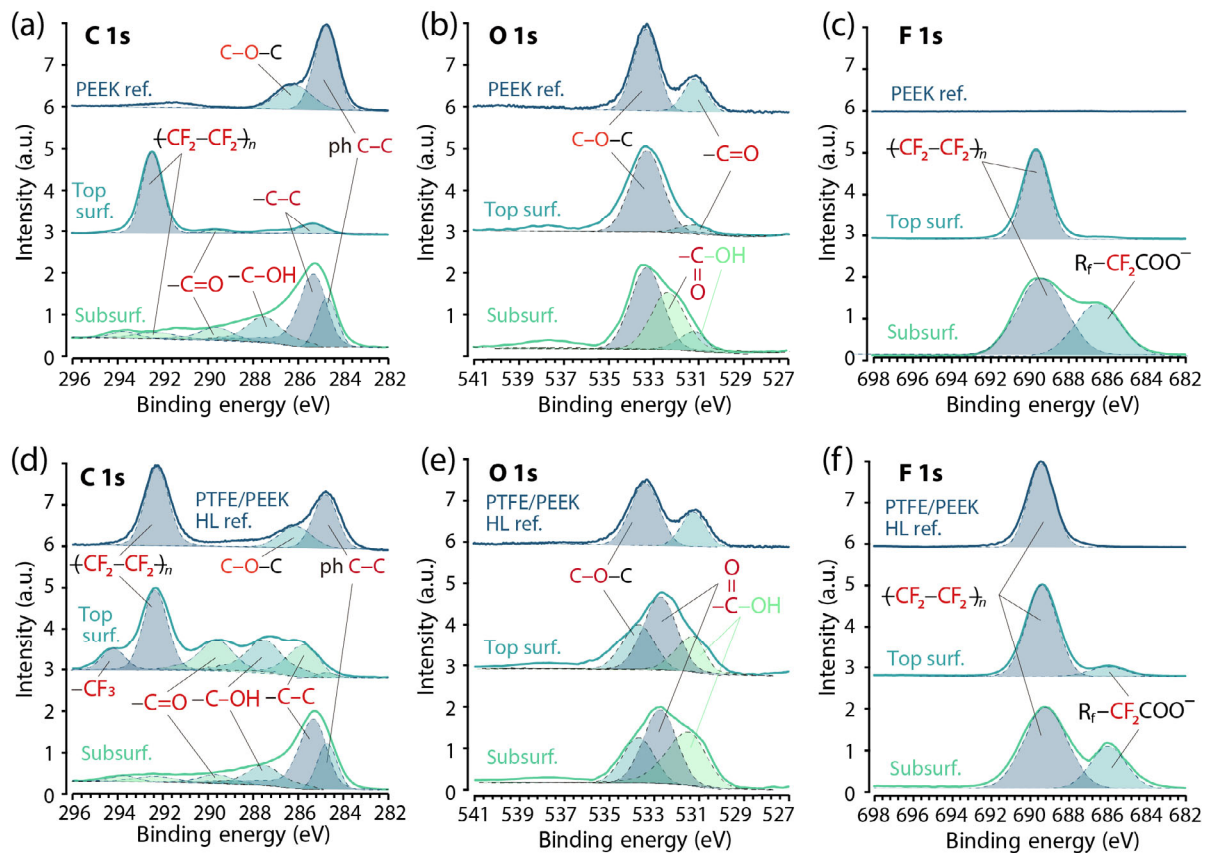


Fig. 9 High-resolution XPS spectra of (a) C 1s, (b) O 1s, and (c) F 1s measured on unworn PEEK reference (ref.), top surface (Top surf.), and subsurface of worn PEEK counter-sample (Subsurf.). High-resolution XPS spectra of (d) C 1s, (e) O 1s, and (f) F 1s measured in unworn PTFE/PEEK HL (ref.), top surface (Top surf.), and subsurface of worn PTFE/PEEK HL sample (Subsurf.). Note: the ph in (a) is short for phenyl; R_f in (c, f) represents the repeat units of fluorocarbon.

carboxylic acid groups results from a series of tribochemical reactions closely related to the friction-induced break of PTFE. Campbell et al. [15] demonstrated that the presence of carboxylic acid groups improves the wear resistance of the polymer surface by enhancing polar interactions near the tribo-interface. Ye et al. [22] further found that the polarity gradient leads to the stability of ultra-low wear interface using PTFE-based composites.

Based on these results, we suspect that the tribochemically carboxylated PTFE leads to a gradient structure of tribolayers. Carboxylated PTFE acts as the binder between non-polar PTFE and polar PEEK polymer layers, maintaining an extremely stable structure capable of supporting extended sliding at the interface. To better understand this gradient structure, an all-atom model of the tribo-interface was constructed using AtomsK software (version beta-0.12.1, University of Lille), as shown in Fig. 10(a). The molecular dynamics simulation was performed to simulate the shearing of gradient tribolayers, as described in Section 2.4. Figure 10(b) shows the snapshot of tribolayers after 400 ps of shearing. In this snapshot, the PTFE layer near the center is yielding. Meanwhile, the carboxylated PTFE layers are closely adherent to the PEEK layers without large deformation.

The structural energy of packed polymer models are calculated as shown in Figs. 10(c) and 10(d), revealing that the PEEK's E_{int} on the carboxylated PTFE model and the PTFE-on-PTFE model are 29.7 and 11.2 eV/nm², respectively. This indicates that the cohesive strength among PEEK and carboxylated PTFE is higher than that of PTFE-on-PTFE. The easy-to-shear ability of PTFE polymer dominates the shear strength of the gradient tribolayers. On the other hand, the relatively strong interaction between polarized PTFE and PEEK molecules stabilized this gradient structure. In short, the simulation results agree with our hypothesis on the tribolayers' functionalities in the PTFE/PEEK HL structure.

In summary, the formation of large-sized and continued PTFE adsorption films is related to the critical size of polymer transfer through van der Waals interactions. During sliding, the adsorbed PTFE and PEEK asperities interpenetrate due to surface asperity creep. Friction performance of such HL is also affected by the mechanical properties of contact surfaces. Polymer counterfaces with high moduli might show lower friction when the PTFE/PEEK HL is lubricated. The tribochemistry-induced carboxylation of PTFE during the tribological test introduces more polar interactions near the tribo-interface. This makes

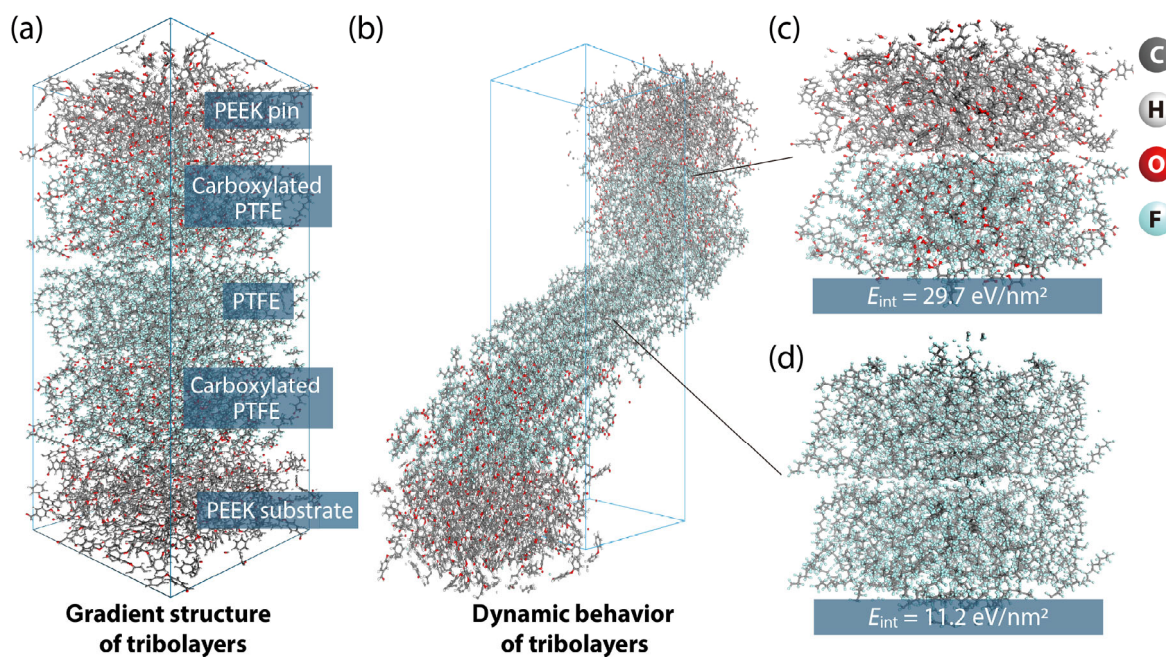


Fig. 10 (a) All-atom model of tribolayer's gradient structure at PEEK against PTFE/PEEK HL interface. (b) Snapshot of gradient tribolayers after shearing of 400 ps. E_{int} of (c) PEEK-on-carboxylated PTFE model and (d) PTFE-on-PTFE model.

the tribolayers form a gradient structure, resulting in ultra-low friction while maintaining great wear resistance of the PTFE/PEEK HL during the tribological test over 140 h.

5 Conclusions

As a new, high-performance solid lubrication method, PTFE/PEEK HL was proposed, prepared, and evaluated for tribological applications. Under comparable testing conditions, PTFE/PEEK HL achieved ultra-low and stable and stable friction coefficients, outperforming the state-of-the-art polymeric coatings or composites by at least 200%. It also has an ultralow steady-state wear rate of $\sim 9.31 \times 10^{-8} \text{ mm}^3/(\text{N}\cdot\text{m})$, a value comparable to those of top-tier ultra-low wear tribosystems in the literature. Mechanistic investigations found that a heterostructured surface was formed as a result of (1) interpenetrating between the PTFE and PEEK from surface asperity creep and (2) friction-induced degradation and polarization of PTFE. Compositional characterizations suggested a tri-layer structure of the tribofilm comprising PEEK, carboxylated PTFE, and neat PTFE closest to the sliding interface. Based on literature hypotheses and MD simulation results in this study, we proposed that (1) tribochemical carboxylation of PTFE increases the polar interaction between friction-modified PTFE and PEEK components and (2) a tribofilm's gradient structure is directly responsible for tribofilm's subsurface stability and surface instability (i.e., low shear strength). In general, the newly proposed HL stands out as an extremely easy-to-implement, surprisingly effective solid lubrication approach that best leverages the mechanistic insights gained by different laboratories around the world from years of research on ultralow wear PTFE composites. The results in this study also reveal great potential of new solid lubrication approach that designs the surface and subsurface independently in the context of high-performance tribofilms.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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